FUNDAMENTAL HYDROGEN TRANSFER STUDIES IN COAL LIQUEFACTION: UNDERSTANDING THE ANSWERS AND QUESTIONS.

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The goal of our research is to quantitatively understand mechanisms of hydrogen transfer pathways between coal-like structures. Understanding the differences between the various hydrogen shuttling mechanisms will yield valuable insight into the fundamental chemistry of coal hydroliquefaction. We have combined experimental model compound studies with theoretical approaches to gain a quantitative understanding of the hydrogen transfer process involving donor solvents that promote the scission of strong bonds and prevent retrograde reactions. Mechanistic modeling has been utilized for the development of a global model for predicting rates of bond scission for one-, two- and three-ring diarylmethanes. The model is tested by thermal model compound studies with labeled donor solvents. Ab initio studies have been utilized to obtain activation parameters for the novel radical hydrogen transfer pathway, and semi-empirical methods have been used to investigate trends within families of both hydrogen transfer and hydrogen abstraction pathways.

Keyword. Hydrogen Transfer.

Introduction.

The classical model of coal hydroliquefaction has evolved from assuming a passive role for hydrogen donor solvents trapping free radicals formed from the thermolysis of labile bonds, to a model that predicts an active role for hydrogen donor solvents participating in the scission of thermal stable bonds.

Fundamental approaches utilizing model compound studies have provided the impetus for evolution of this model as they provide strong evidence for the importance of hydrogen donor solvents in the scission of strong bonds.[1-10] The philosophy of basic research in coal hydroliquefaction is to gain an understanding of structure-reactivity relationships. Understanding why a change in structure results in a change in reactivity will lead to an intelligent approach to improving hydrogen transfer reactions that control both bond-cleaving and bond-forming reactions.

A simplified picture of the units that hold the structures of coal together is summarized in Scheme I. Thermally labile bonds can cleave homolytically to form stabilized radicals (1); arenes linked by longer alkyl chains can decompose by β-scission following hydrogen abstraction (2); and thermal stable diarylmethanes can be cleaved by β-scission following hydrogen transfer from solvent molecules (3). The goal of our research is to understand the role of hydrogen transfer pathways from donor solvents to coal model structures that can result in the scission of this class of strong carbon-carbon bonds.

Scheme I.

$ArCH_2\text{-}CH_2Ar$ -> $ArCH_2\bullet$ + DH -> $ArCH_2\text{-}H$ (1)

$ArCH_2\text{-}CH_2\text{-}CH_2\text{-}CH(\bullet)\text{-}Ar$ -> $ArCH_2\text{-}CH_2\bullet$ + $CH_2\text{=}CH\text{-}Ar$ (2)

$Ar\text{-}CH_2Ar$ + DH -> $Ar(H\bullet)\text{-}CH_2Ar$ -> ArH + $\bullet\,CH_2Ar$ (3)

The role of donor solvent in both the homolysis pathway (1), and the radical scission pathway (2) is generally to trap the incipient radicals to prevent retrograde reactions. On the other hand, the donor solvent participates in promoting the scission of strong diarylmethane carbon-carbon bonds (3).

Several of the model compound studies have focused on identifying and quantifying the competing mechanisms that have been postulated to be important hydrogen transfer steps between aromatic structures. The common denominator of all these works is the dynamic exchange of hydrogen transfer reactions between arene structures. This is not surprising, given the early studies that showed deuterium from labeled solvents can be transferred throughout the coal.[11,12] Hydrogen from the donor solvent, hydrogen gas, and/or from the coal itself is thoroughly scrambled throughout the system. The goal of liquefaction is to have the hydrogen scramble to the appropriate locations to promote bond scission. Thus a fundamental understanding of what controls the hydrogen transfer pathways, from a donor to a receptor, can provide beneficial guidance for experimental process development.

Consideration of both the kinetic and the thermodynamic factors of hydrogen transfer to diarylmethanes leads to two simple questions. *Is hydrogen transfer to the ipso position a necessary requirement for bond scission?* Direct hydrogen transfer to the ipso position of a substituted aromatic ring is both sterically and thermodynamically less favorable than addition alpha to the substituent. *How can we break only the bonds we want to break?* We want to cleave diarylmethanes and leave the alkyl groups alone to increase the formation of liquids and prevent the formation of light gases.

Thermolysis Questions.

Fortunately, an understanding of structure reactivity relationships can lead to some insight to answer these questions. McMillen and Malhotra[1d] have reviewed four possible non-ionic mechanisms of hydrogen transfer that could be responsible for the scission of diarylmethane C-C bonds, summarized in Scheme II: (1) free hydrogen atoms (HA), a two-step pathway involving the scission of a hydrogen from a hydroaryl solvent radical followed by addition to the diarylmethane; (2) reverse radical disproportionation (RRD), involving the transfer of a hydrogen atom from the dihydroarene solvent; (3) addition transfer elimination (ATE), involving a multi-step addition of the solvent radical to the diarylmethane, followed by hydrogen transfer, and elimination; and (4) radical hydrogen transfer (RHT), involving the transfer of a hydrogen atom from a solvent radical to the diarylmethane.

Scheme II.

$ArH\cdot \rightarrow Ar + H\cdot$	
$H\cdot + ArR \rightarrow ArHR\cdot$	HA
$ArH_2 + ArR \rightarrow ArH\cdot + ArHR\cdot$	RRD
$ArH\cdot + ArR \rightarrow ArH\text{-}ArR\cdot$	Addition
$ArH\text{-}ArR\cdot \rightarrow \cdot Ar\text{-}ArRH$	Transfer
$\cdot Ar\text{-}ArRH \rightarrow Ar + ArHR\cdot$	Elimination
$ArH. + ArR \rightarrow Ar + ArHR.$	RHT

Clearly, there is no lack of potential pathways to make diarylmethanes look like weak bonds; an understanding is needed is of what pathways are important under a given set of conditions, and how to optimize the transfer of hydrogens to the appropriate positions that promote bond scission.

These free radical hydrogen transfer pathways are separated into two categories. Because of the product-like (RRD) and reactant-like (HA) nature of the transition state of these two pathways, the activation parameters can be estimated. On the other hand, because of the intermediacy of the transition state of the RHT and ATE hydrogen transfer pathways, the activation parameters are not so easily predicted. For these hydrogen transfer reactions, computational approaches will be necessary to investigate the structure reactivity relationships.[13] The difficulty in assigning a barrier to these pathways has resulted in some debate as to the significance of the RHT hypothesis.[4d,e] Although the RHT pathway was suggested to operate under a limited set of conditions,[1c] it has often been invoked as an important pathway for the scission of a large variety of conditions.[14]

Regardless of the pathway, hydrogen is transferred to the arene structures in the presence of donor solvents. In our current work we are concerned with the fate of adding hydrogen, by any pathway, to a nonipso position and if this can result in the scission of strong carbon-carbon bonds.

We have attempted to devise an experiment to quantify how many hydrogen transfers are required to induce bond scission in diarylmethanes. Thermolysis studies of 1,2'-dinaphthylmethane (1,2'-DNM) in a perdeuterated donor solvent mixture, dihydroanthracene(d_{12})/anthracene(d_{10}) results in the scission of the diarylmethane to yield both naphthalene and methylnaphthalene (ca. 5% conversion, 100 minutes, 400°C). Analysis of the products and reactants by GCMS reveals several interesting observations. The most obvious is the reduction of anthracene by the dihydroanthracene as we previously observed.[4f] Reduction of the 1,2,3,4-positions of anthracene occurs by a series of RRD and hydrogen abstraction steps. Analysis of the remaining 1,2'-DNM shows more deuterium incorporation into the diarylmethane than was expected from exchange at the benzylic positions. Therefore, hydrogen (labeled as deuterium in this experiment) is transferred to the arene rings of the diarylmethane from the donor solvent without the scission of any carbon-carbon bonds. Analysis of the product naphthalene shows that, on average, more than one deuterium is incorporated in the naphthalene cleavage product. If direct ipso hydrogen transfer was the only operating hydrogen transfer mechanism, only one deuterium would have been detected in the naphthalene product. However, because more than one deuterium per scission product was detected, something in addition to ipso displacement must be competing.

This should not be surprising if the probability of adding a hydrogen to the ipso position is considered verses the probability of adding a hydrogen to any other position. To illustrate, consider the case of hydrogen transfer by a reasonably selective mechanism (RRD or RHT), to the ipso position of diphenylmethane. Several factors reduce the probability of ipso hydrogen addition (Figure I). One source of discrimination between the ipso and nonipso positions is the *steric* bulk of the donor, either a dihydroarene (RRD) or a dihydroaryl radical (RHT). Additional *thermodynamic* factors are against ipso addition. The adduct formed by addition of hydrogen γ or β to the ipso position yields a tertiary radical that is more stable than the secondary radical formed by addition to the ipso position. Finally, consideration of *statistics suggests* there are several more nonipso positions, 2,3,4,5 or 6-position. A conservative estimate suggests addition of a hydrogen atom to the nonipso position will occur ten times more frequently than addition to the ipso position. It could even be argued that there is a higher probability that the "less selective" free hydrogen atom pathway will more likely add to the ipso position of a substituted arene because this pathway is least affected by the steric or the thermodynamic constraints.

If, as we have argued, the hydrogen is more likely to be transferred to a nonipso position, to understand the complete picture we must understand the fate of the nonipso hydrogen addition adduct. A more complete scheme of hydrogen transfer, including the addition to nonipso positions, is shown in Figure II. Depending on the reaction conditions, there are two possibilities for the nonipso adduct. At higher donor (dihydroarene) concentrations it is possible to trap the adduct. Abstraction from the solvent to produce a reduced arene, path (e), results in lowering the bond energy of the diarylmethane to the ballpark of the thermally labile diarylethane type bonds.[15] At low donor (dihydroarene) concentration, scission of the hydrogen atom will dominate the radical termination pathways. In this case, although we may not have started with a free hydrogen atom, we may need to account for free hydrogen atom chemistry for a complete picture.

If the nonipso adduct is not trapped something must be done to make efficient use of the hydrogen atom donated from the solvent mixture. One approach that has been used at low donor concentrations is to add a good hydrogen atom trap. Hydrogen atoms add to arenes more readily than abstract from dihydroarenes.[1b,7a] If anthracene is added to the reaction mixture, the hydrogen can be stored for re-use. Radical disproportionation of the hydroaryl radical generates a dihydroarene donor solvent.

It remains to be determined if the excess deuterium observed in the 1,2'-DNM thermolysis studies is due to bond scission by the reduction (pathways b, e, and f) shown in Figure II or due to inefficient hydrogen transfer (pathways b, and d, or RHT, in competing with ipso addition). Answering these questions will provide additional insight into improving the efficiency of hydrogen transfer and best utilization of hydrogen donor solvents.

Catalysis Questions.

It has also been reported that iron catalysts promote the scission of diarylmethanes at lower temperatures than thermal solvent pathways.[16] We have found that alkylarenes are reduced with no apparent loss of the alkyl group. For example, we have found that the catalytic reaction of 1-methylnaphthalene in dihydrophenanthrene results in the formation of 1-methyltetralin; no naphthalene scission product was detected. On the other hand under the same reaction conditions, 1-benzylnaphthalene and its derivatives yield only scission products with no apparent reduction.

Studies investigating the relative rates of bond scission in a series of diphenylmethanes suggest a mechanism that may involve either a two-step, electron transfer followed by reduction of the radical center or a proton transfer from the catalyst to the substituted arene (Figure III). A mechanism involving ipso hydrogen transfer from the catalyst to the arene is tentatively ruled out because we would have observed little selectivity between the scission of either the methyl or the benzyl substituent if hydrogen transfer to the ipso position were rate limiting.[17] We prefer the two-step electron transfer-hydrogen atom transfer mechanism to generate the intermediate cation. Compared to the radical mechanism where the loss of a benzyl radical is only ca.10 kcal.mol lower than loss of methyl radical, there is a substantial difference in scission by the ionic pathway. The difference between scission of a benzyl cation and scission of a methyl cation could be as high as 70 kcal/mol.

Wei et al.[18] have compared the decomposition of dinapthylemthane with the decompostion of dinaphthylethane. A similiar mechanism could be proposed for their hydrocracking catalyst. They only detected scission when a stablized leaving group was present, e.g. dinapthylmethane to naphthalene and methylnaphthalene. In the absence of a stabilized leaving group, e.g. dinaphthylethane, they observed mostly reduction, tetralin derivatives.

Conclusions.

Hydrogen transfer is extremely dynamic. It is hard to imagine a magic catalyst or smart solvent that can selectively add a hydrogen to the ipso position of of a diarylmethane.

Hydrogen will be transferred by one or more pathways several times before finally promoting scission of strong bonds.

We have attempted to answer two questions in our recent work: (1) Is hydrogen transfer to the ipso position a necessary requirement for bond scission? and (2) How can we break only the bonds we want to break? We have outlined a multistep hydrogen transfer scheme, given the high probability of nonipso hydrogen transfer, that results in a reduced diarymethane adduct capable of homolytic scission at coal liquefaction temperatures. Both the catalytic ionic pathways and the thermal reduction pathways permit the scission of stabilized benzylic radicals without requiring the scission of less stabilized alkanes.

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FIGURE I.

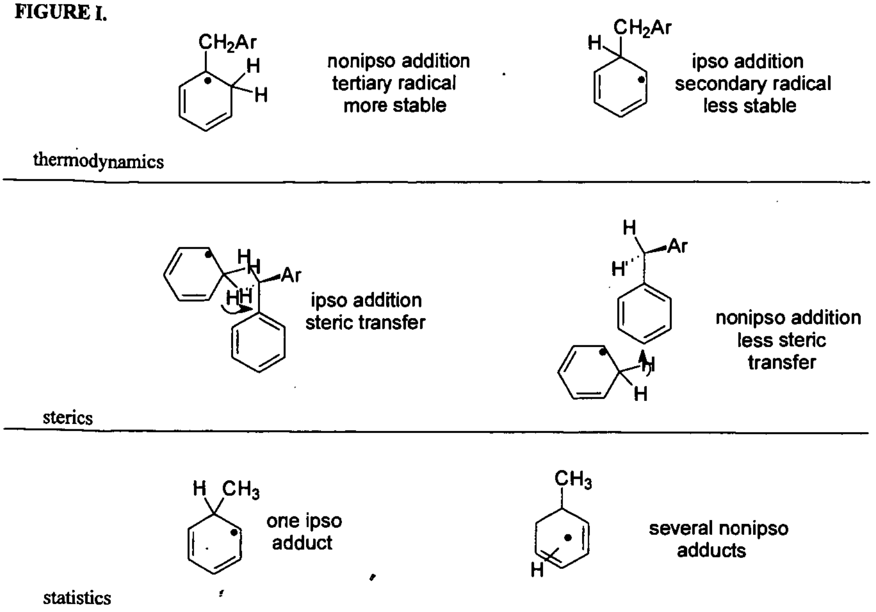

CH2Ar
H
H
nonipso addition
tertiary radical
more stable
CH2Ar
H
ipso addition
secondary radical
less stable
thermodynamics
H
H
Ar
HH
ipso addition
steric transfer
H
Ar
H'
nonipso addition
less steric
transfer
H
H
sterics
H CH3
one ipso
adduct
CH3
H
several nonipso
adducts
statistics

FIGURE II

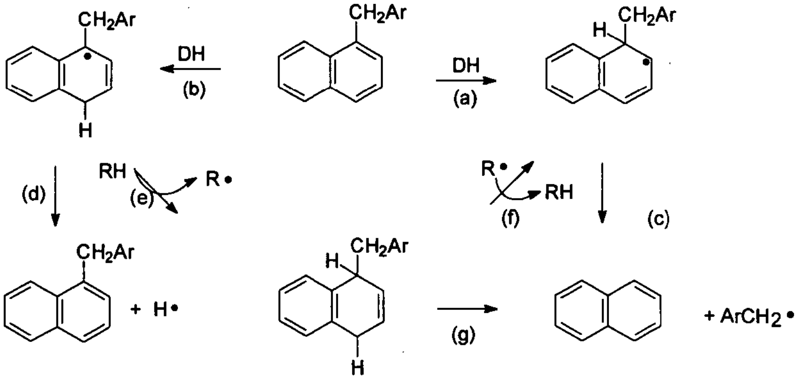
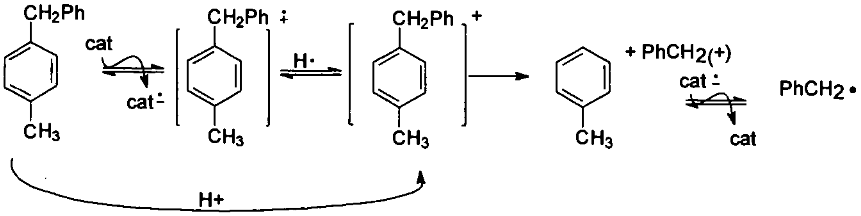

CH2Ar
DH
(b)
CH2Ar
DH
(a)
H CH2Ar
H
(d)
RH
(e)
R•
R•
(f)
RH
(c)
CH2Ar
+ H•
H CH2Ar
H
(g)
+ ArCH2•

FIGURE III


CH2Ph
cat
cat∸
CH3
CH2Ph ∔
CH3
H·
CH2Ph +
CH3
CH3
+ PhCH2(+)
cat∸
cat
PhCH2•
H+

HYDROGEN TRANSFER DURING DIRECT COAL LIQUEFACTION WITHOUT HYDROGEN OVERPRESSURE

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INTRODUCTION

Since the late 1960s, the British Coal Corp. has been concerned with the development of two coal liquefaction processes, both of which depend upon a liquid solvent at low pressure to extract the coal. The first of these was designed to extract a precursor suitable for the manufacture of electrode coke (1). In the second process, the extraction step was modified by the introduction of hydrogen donors into the solvent and employed as the first stage of a two-stage liquefaction process (Liquid Solvent Extraction, LSE) whose net products were distillate transportation fuels(2). Pilot plants of about a ton per day for each process have been built and operated successfully

This paper is primarily concerned with the LSE process and will consider the significance and effects of solvent hydrogen transfer on the performance and operation of the first stage, its influence on subsequent process steps, and on the overall process.

LSE PROCESS DESCRIPTION - A schematic of the process is shown in Fig. 1

Coal is dried, pulverised and slurried with a hydrogen donor recycle solvent. This solvent, which is a mixture of aromatic and hydroaromatic hydrocarbons is produced within the process and is entirely coal-derived.

The coal slurry is pressurised to 20 bar, preheated to the reaction temperature of 410°C and fed to a digestor in which up to 95% of the coal is dissolved. The use of elevated pressure in this stage is to prevent undue vapourisation of the solvent. During the digestion process, hydrogen is donated from the solvent to the coal structure as it breaks up, stabilizing the lower molecular weight fragments and preventing retrograde reactions. The resulting digest contains dissolved coal ('extract'), residual coal solids and the mineral matter originally present in the coal.

The digest is cooled to 300°C, reduced in pressure and filtered to remove the mineral matter and the undissolved coal. The filtrate, which is solids free and has a very low ash content (i.e. less than 0.1%), is known as 'coal extract solution'. The filter cake is washed with a low boiling fraction of the solvent, which displaces the coal extract solution trapped within the voidage of the cake. Residual wash oil is in turn recovered by vacuum drying the filter cake. This washing and drying procedure minimises the loss of extract and solvent with the cake.

In the second stage, the coal extract solution is pressurised, typically to 210 bar. mixed with hydrogen gas, preheated and fed to ebullated bed hydrocracking reactors. These reactors operate at temperatures in the range 400 - 450°C. Standard oil industry heavy residuum hydrodesulphurisation catalysts can be used.

The product from hydrocracking is distilled to recover the recycle solvent (boiling above 300°C) and to give three main products: LPG, naphtha (boiling below 180°C) and mid-distillate (boiling range 180-300°C). In addition, a by-product pitch stream (nominally boiling above 500°C) is taken off, although most of the material in this boiling range is recycled as part of the solvent. The remaining by-product streams contain light hydrocarbon gases, predominantly methane and ethane, and heterogases. An appreciable proportion of the oxygen originally present in the coal is emitted as CO_2, reducing the overall hydrogen consumption.

In addition to the process configuration described above, several alternative processing options have been examined which may be appropriate under some economic conditions. The pitch by-product may be fed to a delayed coker to recover additional distillate and to produce a premium grade coke which is an excellent starting material for the preparation of graphites and carbon electrodes. The rehydrogenation of the recycle solvent to replace the hydrogen donated to the coal during digestion may be carried out in a separate reactor on a fraction of the solvent recovered by distillation from the filtrate. Finally, if saturated hydrocarbon (which are not hydrogen donors) build up in the solvent, a portion of the solvent may be fed to a 'satcracker' in which the saturated compounds are thermally cracked to lower boiling liquids and gases.

The main features of the LSE press which distinguish it from other two-stage direct liquefaction processes are therefore the low pressure first stage and the removal of solids by filtration, both of which reduce capital costs. All coals except anthracites can be processed, although some energy penalties are associated with the use of lignites.

Over the past 25 years the British Coal team of workers have built up expertise in the various unit operations, based partly on practical plant experience and partly on more fundamental laboratory studies, mainly but not solely with bituminous coals.

Although it became apparent that each stage of the process affected the others, this paper will now concentrate on the dissolving (or extraction) stage and in particular upon hydrogen transfer and retrogressive reactions therein.

The aim of most current coal liquefaction processes is to produce distillate fuels in high yield and thus much effort has been expended in trying to minimise retrogressive reactions which eventually lead to coke formation. In contrast in the Electrode-coke process (Fig. 2) maximising the quantity and quality of extract derived coke was the aim; it is thus relevant to review some of the studies of this process to assist understanding of retrogressive reactions.

DIGEST VISCOSITY

Studies of the changes in slurry viscosity during extraction process have shown that, regardless of temperature and solvent to coal ratio, the same general time-dependent pattern was observed(3) for bituminous coals, Fig. 3.

Starting from the slurry (A) there is an initial rise in viscosity (Zone B) which takes place rapidly at all temperatures studied, reaching a peak within a few minutes, possibly within seconds. The peak viscosity in this region is at least five times that of the untreated slurry. Comparison between the physical state of a slurry which consists of 20-25% rigid particles in a fluid (anthracene oil), with that of a digest of large polymers, formed from the dissolving coal, and intimately dispersed within the same fluid, enables the change in viscosity during digestion to be appreciated. It is also known that the coal particles themselves swell prior to their disintegration and this phenomenon too is thought to contribute to the viscosity increase.

After reaching a peak the digest viscosity drops continuously over a period of about 20-30 mins., (Zone C) a time found to be independent of temperature. However, the minimum viscosity reached at the end of this zone was temperature dependent, the higher the temperature the lower the viscosity. This result indicates more extensive depolymerisation at higher digestion temperatures. Furthermore, the initial rate of viscosity reduction was found to increase markedly with increasing temperature. At the lower temperatures studied, the rates of change of viscosity over the same viscosity range can be compared reasonably accurately. The time taken for the viscosity to decrease from 2.5 to 1.5 cP (measured at 250°C) was 20 mins. at 380°C and 5 mins. at 400°C. From these data, an activation energy of 60 kcals/g mole can be calculated, indicative of a process involving the breaking of moderately strong chemical bonds. It was considered that the kinetics observed were the result of the combination of several reactions; however, the cause of the reduction of viscosity is attributed solely to the depolymerisation (i.e. reduction in molecular weight) of the coal extract.

After about an hour (total time) the viscosity then begins to increase again, independently of temperature (Zone D). The polymerisation reactions occurring in this zone which cause the second viscosity increase obviously started before the end of depolymerisation stage and it is the combination of these two reactions that controls the position of the minimum at the end of Zone C. The rate of increase of viscosity is not greatly enhanced between 380 and 420°C indicating a low activation energy for this process which is consistent with polymerisation reactions.

Finally, the reduction in viscosity during Zone E is explained as due to the growth of mesophase in which the higher molecular weight coal extract components are concentrated into many small areas within the remaining fluid which is of lower viscosity, hence creating a relatively dilute continuous phase. The end of zone E represents a slurry of coal extract mesophase in solvent.

It was also realised that beyond Zone E and under exceptionally severe conditions, the whole digest, including solvent, would coke and thus the viscosity would rise again; this is definitely a zone that there is every incentive to avoid in any process!

Assessments of coke properties confirmed that by employing digestion times much longer than those necessary for extraction there was some improvement in final coke quality, presumably because the mesophase liquid crystals had been given time to grow before coking became too advanced. Such a step is now known to be essential to the formation of graphitisable carbons.

The quinoline insolubility of the slurry or digest shows an initial reduction (Zone B & C) as the coal is taken into solution. It then rises in a manner consistent with a 2nd order, polymerisation reaction, i.e. more rapidly as the solvent to coal ratio is reduced.

Several lessons and questions which are relevant to coal liquefaction in general emerge from these studies of the electrode coke process.

(1) to minimise retrogressive reactions then, all other things being equal, a high solvent to coal ratio should be used. In process development there are often strong pressures from design and costing engineers to reduce the amount of recycling solvent which has to be handled for a given coal throughout. Those applying these pressures rarely take into account that small improvements in the overall conversion to liquid products could be more valuable than the cost of increasing the solvent to coal ratio substantially; this is particularly so if the solvent doesn't all have to be distilled.

(2) similarly, as soon as extract is taken into solution it should be diluted with the other liquid phase (i.e. solvent). Presumably small particle size would help in this respect as would agitation that resulted in high particle Reynolds numbers.

(3) if conditions that produce some cokingoccur somewhere in the process after extraction (e.g. in preheaters or on catalyst surfaces) then is it better to allow those species that polymerise more rapidly to do so in the extraction stage, as they will be removed along with the residual coal (e.g. in the subsequent solid-liquid separation step-by filtration in the LSE process), thereby increasing the life of catalyst and preheater.

(4) what is the relative ease of hydrogenation and hydrocracking of molecules that are truly in solution compared with the same species arranged in mesophase liquid crystals? In other words is the irreversible point in inevitable coke formation at the liquid crystal ordering stage or after further polymerisation?

(5) the presence of hydrogen, either as H_2 or in hydrogen donor solvents, is well known to reduce the rate of carbon (strictly it is still only a semi-coke) deposition on catalysts and to dramatically reduce viscosity. This does not mean however that hydrogenated extract doesn't polymerise or form mesophase. Indeed given suitble conditions, bigger and better liquid crystals can be formed resulting in excellent needlecoke because the hydrogenation reactions help to remove some of the heteratoms thereby reducing the steric hindrance to perfect alignment of aromatic layers. This is desirable if coke is aimed to be the end product but the formation of micron-sized mesophase spheres in the digestor, perhaps due to imperfect mixing or just exhaustion of hydrogen donors in the solvent, could cause problems in the solids separation stage due to their plastic deformable nature.

LIQUEFACTION AND H-TRANSFER

The term coal conversion is used with different meanings and can cause confusion. It can mean the extent of conversion into liquid and gas, a secondary solvent, quinoline, cresol or THF, being used to determine the insoluble organic matter (IOM). In other cases conversion is defined as the yield of liquids boiling below say 450°C.

It is reasonably well accepted that little coal will dissolve in most solvents below 200°C (although work with NMP with and without CS_2 can give extensive solution of some coals (4)). However at the temperature of most liquefaction processes, i.e. around 400°C, the majority of most coals (except anthracite) can be taken into solution. Using phenanthrene or recycled anthracene oil without hydrogen over pressure, up to 80% of bituminous coal appears in the filtrate. Much of the extract can be insoluble in THF and some, even insoluble in quinoline which implies molecular weights in excess of 2000.

Is this conversion? One could say that the coal has merely been reconstituted without its mineral matter and some of its macerals, e.g. the inertinite. To support this is the fact that the softening point of such pure extracts is over 300°C, i.e. only a little lower than of the coal; it takes the addition of about 2% hydrogen to reduce the extract softening point to around 150°C (e.g. as in the SRCI process or as has been observed when using tetralin as solvent(7)).

The amount of coal taken into solution is enhanced by the presence of hydrogen, either from a donor solvent or as gas. The molecular weight of the extract is reduced as has just been mentioned, but whether this is instantaneous or caused by a sequential reaction is open to discussion. Is it that the extra taken into solution when donor hydrogen is available is due to the avoidance of very rapid retrogressive reactions by some thermally produced radicals, as is perhaps suggested by recent work, (5), or is it that the hydrogen is contributing directly to the dissolution reaction?

Whatever the reason, there is no doubt that more coal appears in solution when hydrogen donors are available, and that for a given coal the extra conversion is dependent on the amount of hydrogen transferred. Thus it seems reasonable to assume, for the purposes of process development and reactor design, that until proven otherwise, there are two discrete steps i.e. coal solution and liquid phase hydrocracking of the coal extract. In some process designs it all happens in a single reactor whereas in LSE for example the first reactor is primarily for dissolution and the second reactor for hydrocracking. Specific conditions can be chosen for each reactor, rather than the necessary compromise when a single reactor system is used.

COAL EXTRACT QUALITY

Increasing extraction to the maximum possible extent would be desirable if all the coal molecules taken into solution were identical. But bearing in mind the variation of the hydrogen contents of the macerals that make up the bulk coal (e.g. 7% in liptinite to under 4% in some of the so-called "inertinite" that can be dissolved) this is unlikely to be even an approximation of the truth. In deciding whether maximum extraction is the optimum the most important properties of the coal extract molecules are their rate of hydrocracking and the consequent yield of desired product (i.e. gasoline rather than gas), and the hydrogen consumption needed to achieve this. Whilst experimental measurements of the amount of coal going into solution can be quickly and accurately determined experimentally the same cannot be said for the hydrocracking properties just mentioned.

In studies (6) of the reactivities of coal extract solutions, samples were made from different coal preparation plant streams, in which both mineral mater and maceral distribution varied. Although extents of dissolution varied with inertinite content by as much as 10% differences in hydrocracking could not be distinguished because of experimental reproducability. These coal samples were far from pure macerals so it cannot be concluded yet that there aren't differences between maceral extracts from the same coal. All other things being equal, which is rarely the case in coal science, one would consider it desirable to have a high liptinite content in the feed coal because of its high hydrogen content. Unfortunately a lot of this hydrogen is in alkyl groups and probably results in higher yields of less valuable gaseous products.

Overall it should be mentioned that advantage could be taken of modern dense media coal cleaning technology in a commercial liquefaction plant with the clean fraction going to liquefaction and the middlings fraction to utilities. As shifts of small amounts in the extent of conversion (whether it be to extract or to finished products) have very significant effects on plant economics, it is still desirable to do further work quantifying the magnitude of any difference between maceral extracts.

SOLVENT QUALITY

In any plant the solvent has to be recycled and thus although useful studies can be performed using pure compounds and doing once-through i.e. single cycle, experiments, eventually recycle must be studied. Whilst the biggest change takes place over the first recycle, changes can continue for a long time as the solvent becomes truly process-derived. Monitoring and then controlling these changes can present a big challenge.

In experimental work a 102% solvent mass recovery should be aimed for to allow for overall losses that are likely to occur even with the most rigorous housekeeping. If there is a slight solvent surplus then it can be converted into lighter products without much effect on plant economics; if there is a solvent deficit the process isn't viable.

In most liquefaction processes, including LSE, the process solvent consists of material boiling above 300°C and includes some above 500°C (which is extract that is not 'converted' during hydrocracking). From studies with various pure compounds and process solvents particularly hydrogenated phenanthrenes and pyrenes, it has been concluded that di- and tetra hydro-derivatives are the most reactive and that they are preferred to the extensively hydrogenated species (i.e. the hexa or octa hydro-derivatives). It is thus preferable to have every molecule hydrogenated to a small extent rather than a few heavily hydrogenated species. As the maximum amount of hydrogen transferred to the coal during extraction is only 1 - 2% of coal, this represents less than 1% on a solvent basis (equivalent to that which can be provided by di-hydro species of aromatics boiling between 300°C and 500°C). The levels of hydrogen donors should of course be above the minimum so that even at the end of the digestion stage there is still a concentration of hydrogen donors available to cap further radicals that are formed by continuing albeit slower thermal cracking of coal and extract molecules.

Not all the hydrogen donated by the solvent reaches the desired recipient, i.e. the extract. About a tenth ends up as molecular hydrogen and represents an inefficiency. If catalyst is present it merely enhances solvent dehydrogenation and thus increases the yields of IOM and hydrogen. The hope that catalyst might enable hydrogen to be released from the solvent at an appropriate rate to match coal radical formation has not been realised. This is perhaps yet another indication of the difficulty of having coal, hydrogen and catalyst and maybe solvent simultaneouly present at the same reaction site.

MONITORING RECYCLE SOLVENT

While proton NMR has proved extremely useful for monitoring short term changes during dehydrogenation (i.e. extraction) and rehydrogenation it is, however, not so good for estimating absolute concentrations of hydroaromatics. Generally, the use of NMR is limited for tracking if there is the possibility of slow long term changes in the solvent composition. In plant operations another reason to aim for 102% solvent recovery is as a way of limiting the build up of undesirable trace species in the solvent.

It is also necessary to have a method of determining if the extracting power of the solvent is decreasing before the point is reached when plant filter cake yields rise and other operational problems due to insufficient hydrogen transfer set it. Remedial action, e.g. by increasing hydrogenation or sat-cracking, would then have a chance of recovering the situation.

Early in the LSE project this need was especially pressing in convincing a potential sponsor that the LSE process could cope with their lignite and the author promised to devise such a test in time for the recycle run due to take place a few months later. So was born SDI, or Solvent Dissolving Index to give it its full name.

The test (7) involves diluting by a known amount a sample of the solvent with a non-hydrogen donor (usually, but not necessarily, naphthalene) so that there are less hydrogen donors than required to ensure maximum extraction when a mini-bomb test is done with this diluted process solvent.

Tests for the particular coals in use with well characterised solvents enable calibration graphs to be constructed Fig. 4 & 5 in which nominally an SDI of 10 means that there are just enough hydrogen donors to ensure maximal extraction

In practice it was found that a certain margin above this minimum was desirable, i.e. 3 or 4 but the SDI fulfilled its major objective of enabling the changes in recycle solvent donor properties to be confidently monitored. As with testing coals the best test of a solvent is to perform an actual extraction.

Non distillate fractions of recycle solvents (i.e. pitch) were shown to be excellent solvents, those with softening points under 200°C having SDI's greater than 10. Such pitches have little hydrogen donor ability and contain plenty of coke precursors so that when used alone extractions reduce if severe digestion conditions are used (i.e. above 420°C). However, as they are normally diluted with distillate material this is rarely a problem and keeping a certain level of pitch in the recycling solvent became generally regarded as advantageous, helping to keep everything in solution, being intermediate in MW etc between solvent and extract, but compatable with both.

At almost the opposite extreme are the light end saturates which are basically not hydrogen donors. The alkanes which usually represent about a quarter of these are thought to be formed directly from the coal. For Point of Ayr coal this is about 0.3% coal (8) whereas for the lignites it can be much greater. The others, i.e. naphthenes, are formed in the hydrotreatment stage and once formed are difficult to dehydrogenate, as was found in many attempts to achieve this catalytically. It was found, however, that if only aromatics and naphthenes were present then the naphthenes did donate some hydrogen and extraction levels above that expected from the pure aromatics were achieved (9). However, hydroaromatics donate their hydrogen first and the naphthenes later, if at all. Various ways of trying to utilise this interesting effect were considered but none proved practical.

CONCLUSION

In order to achieve maximal coal extractions and to minimise retrogressive reactions of the extract, the recycle solvent must be in adequate supply and of the right properties, i.e. good hydrogen donor ability as well as good physical solvent properties.

It is noteworthy that during the 70's and 80's other liquefaction process developers, who without exception used high pressure hydrogen during extraction, gradually came round to the view that having a 'good' solvent present made their processes work better, i.e. "hydrogen donor species could reach places that ordinary (gaseous) hydrogen could not".

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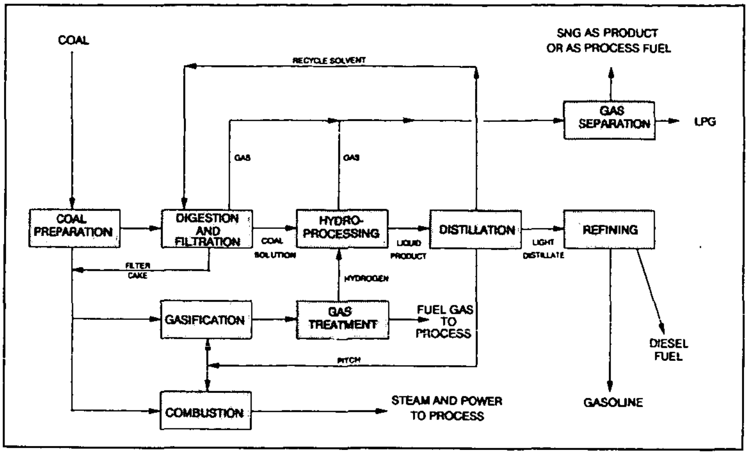
COAL
SNG AS PRODUCT OR AS PROCESS FUEL
RECYCLE SOLVENT
GAS SEPARATION
LPG
GAS
GAS
COAL PREPARATION
DIGESTION AND FILTRATION
COAL SOLUTION
HYDRO-PROCESSING
LIQUID PRODUCT
DISTILLATION
LIGHT DISTILLATE
REFINING
FILTER CAKE
HYDROGEN
GASIFICATION
GAS TREATMENT
FUEL GAS TO PROCESS
DIESEL FUEL
PITCH
COMBUSTION
STEAM AND POWER TO PROCESS
GASOLINE

Figure 1 The Liquid Solvent Extraction Process

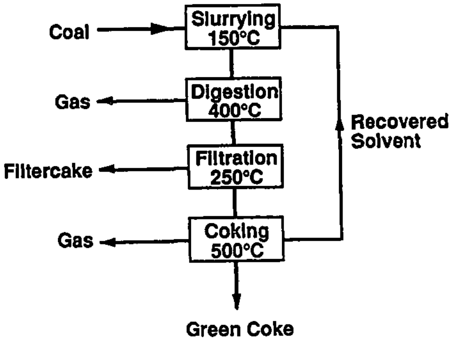
Coal
Slurrying 150°C
Gas
Digestion 400°C
Recovered Solvent
Filtercake
Filtration 250°C
Gas
Coking 500°C
Green Coke

Figure 2. Electrode Coke Process

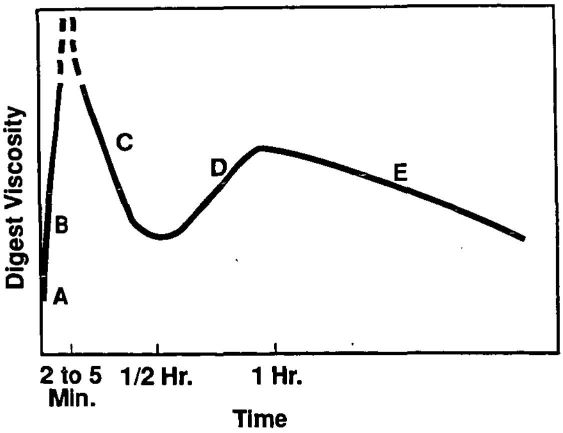

Figure 3. Effect of Digestion Time on Viscosity

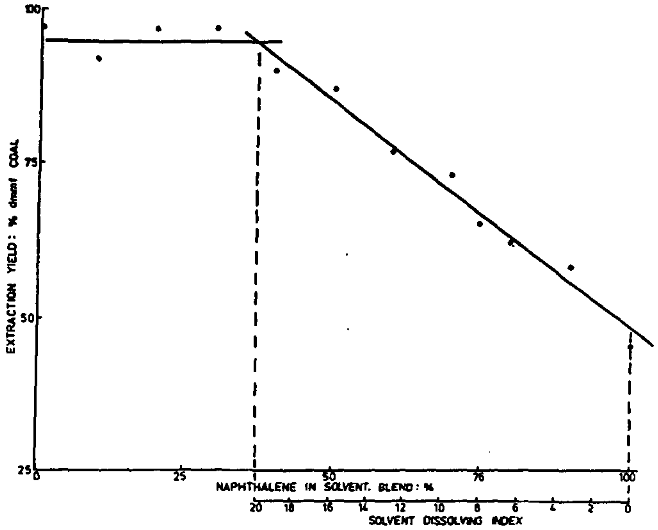

FIGURE 4. SDI CALIBRATION FOR THE LIGNITE

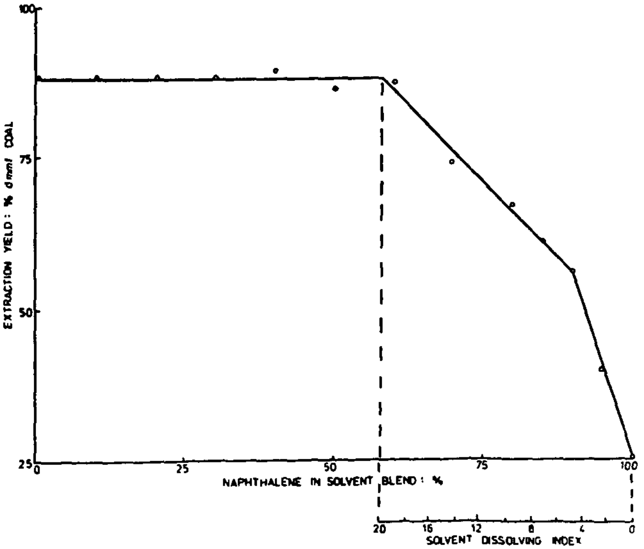

FIGURE 5 SDI CALIBRATION FOR THE BITUMINOUS COAL

THE ROLE OF RECYCLE OIL IN DIRECT COAL LIQUEFACTION PROCESS DEVELOPMENT

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Keywords: Coal, Liquefaction, Recycle Oil

ABSTRACT

It has long been recognized that use of a recycle oil is a convenient and perhaps necessary feature of a practical direct coal liquefaction process. The recycle oil performs a number of important functions. It serves as a vehicle to convey coal into the liquefaction reactor and products from the reactor. It is a medium for mass and heat transfer among the solid, liquid, and gaseous components of the reactor inventory. It can act as a reactant or intermediate in the liquefaction process. Therefore, the nature of the recycle oil can have a determining effect on process configuration and performance, and the characterization of recycle oil composition and chemistry has been the subject of considerable interest. This paper discusses recycle oil characterization and its influence on the industrial development of coal liquefaction technology.

EARLY GERMAN TECHNOLOGY

In the early 1900s, Bergius used a petroleum "heavy oil" as a vehicle to slurry coal in batch and continuous unit liquefaction experiments.[1] The German technology utilized in the 1940s was based on further development of the Bergius-Pier process, and utilized high temperature and pressure (750 K, 300 atm) and an inexpensive (and relatively low-activity) iron oxide catalyst (red mud) in a liquid (sump) phase reactor. The recycle solvent was a distillate from gas phase hydrogenation of the sump-phase reactor overheads. Although this technology anticipated the dispersed catalysts under development today, the process employed a high reaction severity, rather than seeking to minimize reaction severity by improved catalyst or solvent activity.

CONSOL SYNTHETIC FUELS PROCESS

In the 1960s, Consolidation Coal Company sought to improve on the performance of the German liquefaction technology by utilizing more active supported-metal hydrogenation catalysts in fixed bed reactors. To overcome catalyst deactivation problems, the coal dissolution and catalytic conversion steps of the two-stage CONSOL Synthetic Fuels (CSF) process[2] were separated by an interstage deashing step. The coal dissolution step was non-catalytic, and carried out at a relatively low temperature to produce an "extract" suitable for catalytic upgrading. The process was designed to produce a distillate hydrogen donor solvent in the second stage.[3] The role of recycle solvent was explored in bench-scale tests supported by mass spectrometric and ^{1}H- and ^{13}C- nuclear magnetic resonance analysis of the recycle solvent.[4] This work showed that, although the recycle oil increased in molecular weight upon recycle, it became less aromatic (Table 1). Recycle oil characterization was used to indicate the approach of the process operation to steady state, and revealed the important effect of solvent characteristics on other process operations, particularly solids separation.

SOLVENT REFINED COAL PROCESS

In the mid-1970s, interest grew in the development of a process to convert coal into a fuel-oil substitute for use in oil-fired electric utility boilers. The Solvent Refined Coal (SRC) process was piloted by Gulf at Ft. Lewis, WA,[5] and by Southern Company Services (and later EPRI) at Wilsonville, AL.[6] The objective of the process was to solubilize coal under hydrogen, but in a non-catalytic reaction, so that the ash-forming minerals, including pyrite, could be removed by physical means. Some organic sulfur removal also was expected. The deashed products were distilled to yield the SRC product and a distillate recycle solvent. One objective was to produce only enough distillate to remain in solvent balance. This would ensure the maximum yield of the desired SRC product, while minimizing hydrogen consumption.

Because the SRC process was designed as a thermal distillate-recycle process (perhaps aided by the catalytic effect of the coal ash), the operating conditions had to be chosen to achieve satisfactory coal conversion, SRC yield, and desulfurization, while maintaining an adequate yield of recycle solvent. In practice, this proved to be a difficult balance to achieve. Higher reaction temperature tended to improve coal conversion and reduce SRC sulfur, but increased gas make at the expense of recycle solvent and SRC yield.[7]

In addition, because the distillate yield in the SCR process was low (typically, less then 5 wt % MAF coal), the replacement rate of the recycle solvent was low, and changes in solvent composition over time were difficult to assess. Because it was run at relatively constant conditions for long periods of time, and because of its size, the 6 TPD Wilsonville pilot plant became an excellent source of coal liquefaction data and samples for assessing the longer term effects of coal liquefaction on recycle oil quality. In 1977 and 1978, we obtained three relatively large and representative samples of the recycle distillate from Wilsonville for use in bench-scale liquefaction research. Some of the solvents were catalytically hydrogenated in a bench scale unit. These samples were the basis for an extensive characterization effort,[8] which included ^{1}H-NMR and ^{19}F-NMR (for phenol determination following derivatization), GC/MS, FIMS, reverse phase liquid chromatography, and empirical tests of solvent quality.

As the distillate recycle solvent in the SRC-I process evolved (Tables 2 and 3), it increased in total hydrogen content, but was lower in molecular weight, more aliphatic, and more phenolic. The practical consequence, as indicated by the microautoclave solvent quality tests, was that it lost hydrogen donating ability. The underlying structural changes were revealed by the NMR and FIMS data. The overall decrease in aromaticity was totally at the expense of the condensed aromatic structures; uncondensed aromatic hydrogen actually increased. The increase in aliphatic hydrogen appeared in both cyclic and aliphatic regions initially, but as the solvent further evolved, the cyclic aliphatic hydrogen decreased. The apparent loss of hydrogen donor activity under kinetic control (KIN test) was associated with the decrease in condensed aromatic hydrogen. The decrease in conversions at the EQ conditions, designed to measure donor hydrogen content, was associated with the ratio of cyclic to alkyl aliphatic hydrogen. FIMS analysis (Figures 1 and 2) showed that catalytic hydrogenation of the more aromatic solvent (8/77 sample) converted aromatics to hydroaromatics and improved solvent quality. Although solvent evolution increased hydrogen content (and alkyl tetralin) by an amount similar to catalytic hydrogenation, it decreased the concentration the aromatics and the corresponding hydroaromatics.

SELECTIVE RECYCLE AS AN IMPROVED LIQUEFACTION OPTION

The research on the evolution of the SRC distillate solvent clearly indicated the importance of higher molecular weight hydroaromatics as hydrogen donor solvent components. However, the low distillate yield in the SRC process provided few options for improving the situation, leading to the conclusion that recycle of vacuum bottoms, or a vacuum-bottoms component, would be necessary to maintain solvent quality[8]. This concept was tested by separating the SRC into "light" and "heavy" components and using the light SRC (LSRC) as a component of the recycle solvent in bench scale and microautoclave liquefaction experiments.[9] In the microautoclave experiments, the LSRC was added to the Wilsonville solvent sample during 4/78. The addition of LSRC improved solvent quality at the "Kinetic" conditions (Table 4), but decreased conversion at the "Equilibrium" conditions indicating that it contained active hydrogen donors, but not in large concentration. The improvement seen at the EQ conditions under hydrogen pressure were somewhat surprising and the degree of improvement was remarkable. These results clearly indicated that this non-distillate oil was capable of facilitating gas phase hydrogen utilization for coal conversion in the absence of an added catalyst.

THE ROLE OF PARAFFINS IN SOLVENT QUALITY

Not all solvent quality effects can be ascribed to the activity and concentration of hydrogen donors. There has been a tendency to think in terms of "average" structures in describing coal and coal products. However, coal liquids are much more heterogeneous than an average structure might suggest. One feature of solvent quality that the FIMS data, failed to reveal was the concentration of straight-chain and branched paraffinic components in recycle oils; FIMS is relatively insensitive to paraffins. In one case, the recycle distillate from a Wilsonville ITSL run with subbituminous coal produced a 47% wax yield upon ketone dewaxing; 12 wt% of the recycle distillate consisted of n-paraffins.[10] Simple physical removal of this wax fraction increased the solvent quality in the EQ microautoclave test from 71% to 87%.

SINGLE STAGE CATALYTIC LIQUEFACTION

The H-Coal process employs a single ebullated-bed reactor to convert coal to distillate products. In PDU and pilot plant development, a relatively high reaction temperature (825-840 °F) and resid recycle were used to achieve high conversion while minimizing reactor residence size. Compared to the SRC process, H-Coal approached a steady state recycle composition quickly[11] because of the higher turnover rate of the recycle oil components. The process solvent increased in aromaticity and phenolic -OH content with run time, corresponding to catalyst deactivation. Characterization of the recycle oil during the PDU runs was used to determine the approach steady state composition. The results indicated that the residual recycle components, particularly the preasphaltenes, reached a consistent composition relatively early in the run, but the degree of hydrogenation of the recycle distillate decreased throughout the run. This suggested that the rate of catalyst deactivation was relatively more rapid for the larger resid molecules than for the smaller distillate molecules.

INTEGRATED TWO-STAGE LIQUEFACTION

The idea of separating the coal dissolution and catalytic upgrading functions was further evaluated in the development of the Lummus Integrated Two-Stage Liquefaction Process. The Lummus ITSL process used a short-residence-time (SRT), high temperature (850 °F) coal conversion stage, followed by anti-solvent deashing. The deashed oil was converted to liquid products in an expanded-bed catalytic reactor (LC-Finer), which was operated at a lower temperature (720-750 °F) than the H-Coal reactor. The recycle oil from the second stage contained distillate and unconverted resid. Because of the thermal first stage, solvent quality was an important factor in process performance. The reactor configuration also provided an opportunity to investigate the separate roles of catalytic and thermal reactions in direct liquefaction. Comparison of the process oil characteristics in the Lummus ITSL process to those from single-stage H-Coal process were particularly instructive.[12] The results showed that hydrogen donor solvent quality was a key to coal conversion in the SRT first stage, and promoted thermal resid conversion in both stages. The lower temperature of the LC-Finer, compared to that of the H-Coal reactor, produced a more highly hydrogenated resid that underwent considerable thermal conversion in the short-residence-time, high temperature first stage. The temperature of the LC-Finer also contributed to the maintenance of distillate solvent quality by minimizing cracking and isomerization reactions that could remove hydroaromatics and their precursors (Table 5). Most of the development work for ITSL was done with mid-continent bituminous coals, and a limitation was revealed when the process was applied to subbituminous coals. Despite the good solvent quality, coal conversion was kinetically limited, necessitating the use of a longer residence time in the first stage reactor. The Lummus work also demonstrated that interstage deashing was not necessary to maintain catalyst activity, because catalyst activity loss was primarily a function of carbon deposition, which occurred regardless of the presence of solids.

Extensive further development work was done on the two-stage process at the Wilsonville pilot plant, in a wide variety of configurations.[13] The Wilsonville operators concluded that it was necessary to use a dispersed iron oxide catalyst to achieve satisfactory conversions with subbituminous coal. Essentially all of the work with bituminous coals was done with two ebullated-bed catalytic reactors in series. Moderate reactor temperatures, low space velocities, and high catalyst replacement rates (relative to H-Coal), and close-coupling of reactor stages (i.e., no interstage deashing) resulted in improved yields, product quality, and selectivity. The use of a critical solvent deasher (ROSE-SR) unit allowed considerable flexibility in controlling recycle composition. The plant employed high recycle rates of heavy distillate (>750 °F IBP), resid, and unconverted coal to reduce the required per-pass conversion level. The result of these changes was a departure from the original two-stage concept of separating thermal coal dissolution and resid upgrading. Most of the feed to the first stage was recycled resid.

Subsequent work has shown that the insoluble organic matter (IOM) in the recycle resid from Wilsonville is reactive for further conversion, and methods to improve solvent quality by dewaxing and hydrogenation are being evaluated.[14] This work will provide the opportunity to better define the role of recycle solvent quality in the current generation of two stage catalytic liquefaction processes.

CONCLUSIONS

This paper was not intended as a comprehensive review of the subject of recycle oil chemistry, but rather as a perspective on the changing perception of the role of recycle or solvent-mediated phenomena in direct liquefaction process development. In the earlier US work on direct liquefaction, the goal of separating the thermal coal dissolution and catalytic distillate production steps led to process configurations that relied on hydrogen donor solvents for coal conversion. Research showed that the distillate recycle solvents which evolved under mostly thermal conditions were poor hydrogen donors, but that selective recycle of higher molecular weight components improved both donor content and activity. When it was realized that interstage deashing had little practical benefit, conversion of the coal in a catalytic first stage diminished the perceived need for an active hydrogen donor solvent. For subbituminous coals, donor solvent hydrogen alone did not appear to be adequate to achieve satisfactory conversions, leading to the use of dispersed catalysts, greater reaction severity, and solids recycle. However, the improvements of two-stage liquefaction came at the expense of reduced space velocity and increased catalyst usage. Current research is looking to replace the supported-catalyst systems with dispersed catalysts that offer higher selectivity and activity, while avoiding the capital cost of a supported-catalyst system. As this research and development continues, it will be important to understand and evaluate the role of vehicle solvents, and to look for opportunities to utilize solvent-mediated reactions as part of a overall strategy for reducing the cost of producing liquids from coal.

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Table 1. Proton Distributions of Recycle Solvents in the CSF Process

	H-Distributions, Normalized			
	Aromatic	Alpha	Beta	Gamma
Cycle 1	50	39	9	2
Cycle 2	49	35	12	3
Cycle 3	43	37	16	4
Cycle 4	40	37	16	6

Table 2. Characterization of Recycle Solvents from Wilsonville SRC-I Operations

Sample Date	Hydrogen, wt%					– OH meq/g	Solvent Quality	
	Total	Aromatic		Aliphatic			KIN	EQ
		Condensed	Uncond	Cyclic	Alkyl			
8/77	8.0	2.15	0.90	1.96	2.99	1.23	81.4	76.5
4/78	9.0	1.31	0.95	2.29	4.45	1.51	76.5	74.4
10/78	8.9	1.21	1.09	1.99	4.61	1.66	75.4	67.4
Hydro (8/77)	6.9	1.89	0.83	2.54	3.64	0.68	80.9	85.8

Table 3. Comparison of Wilsonville Solvents by FIMS

	Differences, mol % of total liquid	
	Batch VI – Batch I	Hydro – Batch I
Naphthalene	–0.9	–2.1
Tetralin/Indans	4.8	3.1
Mass 178	–3.1	–1.5
Hydro Mass 178	–1.9	2
Mass 202	–1.1	–0.6
Hydro Mass 202	–0.7	1.3
Carbazole	–0.1	
Quinolines		–1.1
Hydroquinolines		0.3
Indanols	1.3	–1.4
Phenols	5.9	–0.2

Table 4. Effect of Kerr–McGee Light SRC addtion on Wilsonville solvent quality (4/78 sample)

LSRC wt%	H2 psig cold	Solvent Quality	
		KIN	EQ
0	0	76.5	74.4
25	0	79.1	73.7
50	0	88.6	65.5
25	1000	85.6	82.8
50	1000	87.6	86.2

Table 5. Comparison of Lummus ITSL (Run 2SCT9) and H–Coal (PDU Run 9) Recycle Distillates

	Concentration, wt%	
	ITSL	H–Coal
Aromatics	12	8
n–Alkyl Aromatics	10	20
Hydroaromatics	31	8
Cyclo–Penta Arom	6	18
n–Alkanes	1	6

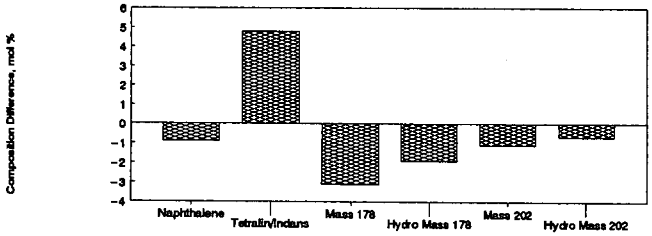

Figure 1. FIMS Comparison: Batch VI–Batch I.

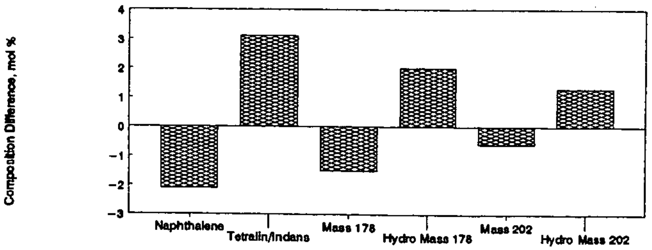

Figure 2. FIMS Comparison: Hydro I–Batch I.

THE ROLE OF THERMAL HYDROGEN-TRANSFER PROCESSES IN CATALYTIC COAL LIQUEFACTION

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Keywords: Liquefaction mechanisms, bond cleavage, iron-catalysts

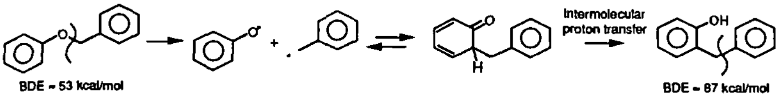
INTRODUCTION

The complexity of coals and their liquefaction products unavoidably means that no "model compound" system can be found that even remotely approaches the real coal in behavior, without also approaching it in intractability of chemical analysis. Notwithstanding these limitations, much has been learned by detailed examination of coal liquefaction phenomenology in light of the behavior of "model" or surrogate structures under liquefaction conditions. Recently we have reviewed[1] some of our own research and other related work that highlights some of what has been learned following this approach. That review summarizes some of the limitations of the formerly accepted weak-bond scission view of donor-solvent coal liquefaction, along with the improved interpretation that emerges when the role of solvent-mediated H-transfer in *actively* promoting bond scission is considered. In addition, the preceding papers in this symposium have highlighted various hydrogen-transfer mechanisms and some key features (and questions) that have evolved during the development of direct coal liquefaction processes.

In this paper, we attempt to build on the background of model compound studies and process development results. We begin by emphasizing two points that have sometimes been lost in discussions of radical reaction mechanisms of hydrocarbon structures. First, high-temperature reactions of coals are not necessarily limited to processes that are purely free-radical: the polar functional groups on coals make it very likely in fact that reactions involving charge separation (i.e., "ionic" reactions) can play some key roles in high temperature coal conversion processes. Second, we assert "thermal" and "catalytic" reactions should *not* be considered as two separate realms of the universe, but as classes of reactions that are *both* important in virtually all catalytic liquefaction processes. Bearing these two points in mind, we then briefly examine some data from the recent literature in an attempt to gain new insight about how cleavage intermediates on iron-based catalyst surfaces may relate to those present in the bulk donor solvent.

IONIC REACTIONS IN BOND-FORMATION AND BOND-CLEAVAGE

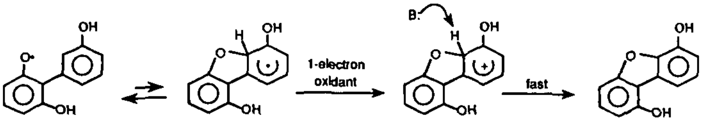
Potential Role of Charged Species and Proton Transfer in Retrograde Reactions. Contrary to the common perception, simple radical recombination reactions are not good candidates for the retrograde processes that plague coal liquefaction, because radical recombination will involve the most stabilized radicals, to generate only the weakest bonds. However, a major exception to this generalization is the case of phenoxy- or other aryloxy radicals. In this case we have suggested[1] that successful retrogression is possible because the highly unstable intermediates generated by ring-recombination of aryloxy radicals are able to rapidly tautomerize through facile intermolecular proton-transfer reactions,[2] thus locking the original unstable recombination into place. This suggestion is illustrated in Scheme 1 with benzylphenyl ether, and its validity is supported by the reports in the literature[3] that the presence of scavengers can decrease, but not easily eliminate, the formation of benzylphenol .



Scheme 1. Retrograde Reaction via Phenoxy Radical Recombination and Rapid Tautomerization.

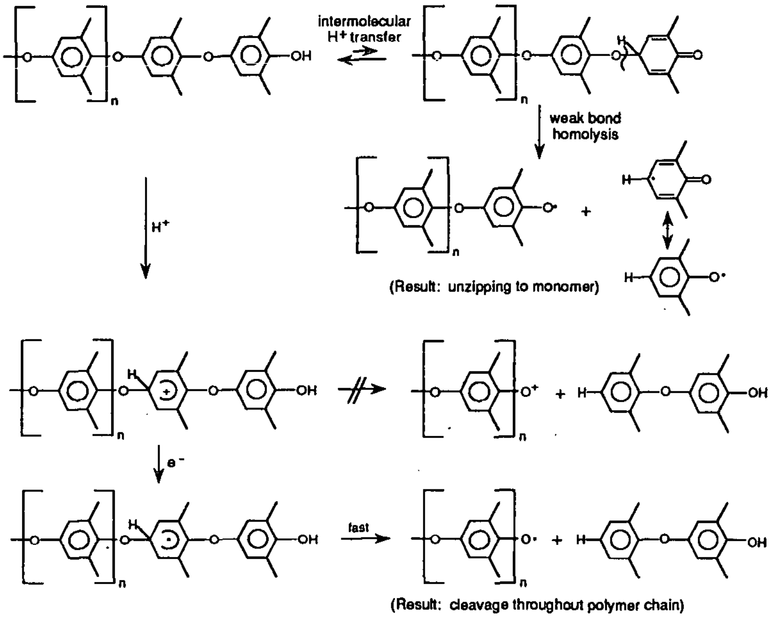
This reaction is one example of interplay between radical and ionic reactions, a phenomenon that may be commonly important in the retrograde processes of oxygen-containing coal structures.

Retrograde Reaction Facilitated by Electron- and Proton- Transfer. The presence of one or more phenolic groups can also promote retrograde reactions that begin with radical addition to an aromatic system. Here removal of the ipso hydrogen is likely enabled not by the relatively high acidity of a keto structure such as in Scheme 1 above, but by the fact that ortho- or para -OH groups on the ipso radical may facilitate its oxidation to the corresponding cation. The cation is very acidic, and can lose a proton extremely rapidly, as suggested[4] for the products observed in the retrograde reactions of dihydroxyarenes and illustrated in Scheme 2.



Scheme 2. Suggested Completion of Retrograde Reaction by One-Electron Oxidation and Proton Loss.

Bond Cleavage Promoted by Electron- and Proton Transfer. Ten years ago, Solomon and Squire showed[5] that pyrolysis of poly(2,6-)xylenol in the inlet of a field ionization mass spectrometer results in a rapid, apparently autocatalytic process at about 380°C, yielding a series of oligomers consisting primarily of monomer through hexamer. The carbon-oxygen bond strength in this polymer is about 77 kcal/mol,[6] far too high to react by simple homolysis at a substantial rate at 400°C. The decomposition of the polymer appears to be predominantly, ***but not exclusively***, an unzipping process, since the monomer is in moderate excess over higher oligomers until the final stages of the decomposition process. The reaction is autocatalytic, accelerating as the phenolic products accumulate. Since the reaction proceeds even in the absence of a donor solvent, generation of the main products (which is a reduction process) must be fed by hydrogen from some minor product(s), presumably non-volatile charry material. These factors lead us to suggest the dual-pathway mechanism shown in Scheme 3.


intermolecular
H+ transfer
OH
H
O
n
weak bond
homolysis
O•
+
H
(Result: unzipping to monomer)
H+
O+
e⁻
fast
(Result: cleavage throughout polymer chain)

Scheme 3. Suggested Cleavage of Polyxylenol via Proton- and Electron Transfer.

The unzipping process by which the terminal units cleave off to form xylenol is almost certainly the reverse of the phenoxyphenol cleavage we reported some years ago, i.e., the reverse of the retrograde reaction shown in Scheme 1 above. However, reaction via the keto tautomer is not the only significant bond cleavage process, since the homolysis of the much weaker[7] (ca. 40 kcal/mol) cyclohexadienone-oxygen bond would be about 10^7 times faster (on a per-molecule of original enol starting-material basis) than reaction of the original aryl-oxygen bonds in the polymer. If we consider reaction of polymeric structures of n = 100, we should still see cleavage of the end units dominating by a factor of about 10^5. In fact, for most of the reaction, the monomer dominates over the small oligomers in the product mixtures by factors of only two to three. The degree of accelerated bond cleavage observed here for even the internal aryl-oxygen bonds is far greater than that which has been observed for simple H-atom transfer to diaryl ether from a good donor solvent.[8] Clearly either this reaction mixture is an unusually good source of free H-atoms, which are reactive enough to readily cleave even simple diphenyl ether structures, or there is something about a phenyl ring with ether linkages in both the 1- and the 4- positions that make it quite susceptible to other cleavage pathways.

We suggest the additional bond cleavage pathway to be considered for internal aryl-O linkages in the polymer chain is the proton-transfer, electron-transfer process also shown in Scheme 3. The rationale here is that oxygen substitution on an aromatic ring system facilitates protonation at certain positions, and electron transfer to the protonated segment results in a net H-transfer, bringing about rapid bond cleavage. Protonation at a carbon bearing an oxygen would itself not readily result in cleavage of the C-O bond, since that would involve elimination of a disfavored aryloxy cation. However, electron transfer following the proton transfer would give the ipso-substituted radical, for which ß-scission should then be very facile. In the polymer, there are two oxygens connected to each ring. While one of them deactivates protonation at the ipso position, the other, which is para to that position, promotes it. The para oxygen would also promote simple H-atom transfer, but such H-atom transfer from a good donor solvent to substituted naphthalenes and naphthols is known to be accelerated by factors of only about ten,[4] whereas here oxygen substitution has accelerated cleavage by many orders of magnitude (as compared to diphenyl ether itself).

It is of course speculative to suggest electron transfer without an identified eT agent, but we are not concerned here with electron transfer near room temperature, but at much higher temperatures, and to a positively charged species. The proton transfer that precedes electron transfer could in fact be facilitated by the high acidity of the very class of keto-form retrograde intermediates shown in the examples given in Scheme 1 above. The net result of the proton-transfer, electron-transfer sequence shown in Scheme 3 is an H-atom transfer. The indirect sequence would of course have significance only if it serves to supplant a kinetically hindered direct H-atom transfer, such as radical hydrogen-transfer (RHT) process, that could otherwise not account for the observed cleavage rates.

To summarize the situation for cleavage of the polyxylenol, two cleavage pathways evidently become operative as coal liquefaction temperatures are approached. One, which cleaves off terminal units that have free phenolic groups, almost certainly occurs through ionic tautomerization to a weakly bonded keto form that undergoes rapid homolysis. The second cleaves O-aryl bonds to internal units that have no free -OH groups. The latter process could involve free H-atoms, but more likely we suggest, involves a proton-transfer, electron-transfer process.

The examples shown in Schemes 1 through 3 demonstrate that heteroatom linkages and functional groups are quite likely to bring ionic reactions into play, often in combination with free radical reactions. In the discussion of iron sulfide catalysis that follows, we take as a starting point the corollary expectation that reactions promoted by iron-oxygen-sulfur surfaces might well involve, even for substrates containing no heteroatoms, the formation of ionic or charge-separated species.

THE ROLE OF THERMAL REACTIONS IN CATALYTIC CONVERSION

It is sometimes said that "thermal" reactions, i.e., donor-solvent--coal interactions, become irrelevant as processes evolve towards more effective use of catalysts. This view is first, clearly not correct, and second, belies the potential value of an understanding of thermal process as a basis for addressing the nature of those processes that are clearly catalytic.

A prime example of thermal reactions playing a key role in a "catalytic" process comes from the field of catalytic resid upgrading (including coal-oil coprocessing). Here, it is well recognized[9] that the factor having the largest impact on distillate conversion is temperature, and that the distillate generation processes are primarily thermal, rather than catyalytic. Thus, even though the feedstock in this case is (at process temperatures) a liquid, and has nominal access to catalyst surfaces, most of the reactions that make distillate actually occur in the bulk reaction medium, remote (in molecular terms) from the catalyst surfaces. Thermal distillate formation is in overall terms essentially a disproportionation process, presumably proceeding to a large degree through Rice-Herzfeld H-abstraction—ß-scission chemistry. The distillate materials are derived mainly from the aliphatic portions of the resid molecules, which as they fragment to an alkane-alkene mixture, act as a hydrogen "sponge" and place a severe hydrogen demand on the portions of the resid molecules that are already hydrogen poor. In the absence of more readily available sources of hydrogen, this demand is satisfied by utilizing hydrogen made available from the aromatic centers of the resid molecules, thus driving those PAH towards coke.

Since the distillate formation is largely thermal, it follows that the coke formation that is driven by it is probably also thermal, occurring remote from the catalyst surface. Although the key role of the catalyst is to limit coke formation, what occurs remote from the catalyst surface can only be impacted *indirectly* by the catalyst, that is by "thermal" reactions between the reaction medium and the coke precursors. Thus the essence of catalytic resid upgrading can be summarized by saying it is relatively easy to derive a large fraction of the potential distillate by simply raising the temperature; the key to a more efficient process essentially involves finding the most effective way to supply hydrogen via H_2, catalyst, and reaction medium, thus limiting formation of coke. In other words, efficient, high space-velocity resid conversion requires optimization of the complementary operation of catalytic *and* thermal reactions. Similar arguments can be made for some stages of coal liquefaction.

CLEAVAGE INTERMEDIATES ON IRON- AND IRON SULFIDE SURFACES.

Another sense in which coal-solvent, or "thermal" reactions are relevant to catalytic coal liquefaction lies in current attempts to learn more about the species on iron sulfide catalyst surfaces. These surfaces are now known[10] to promote coal liquefaction and dealkylation of substituted aromatics via intermediates that involve transfer, in some manner, of only a single hydrogen. How might the surface-bound species be similar to (or different from) the intermediates involved in pure solution-phase hydrogenolysis? Are these surface species likely to be free-radical, or is there enough ionic and/or semiconductor character in the critical crystal surfaces or edges to facilitate the formation of charged species?

Several years ago, Wei et al.[10], and more recently, Davis and coworkers,[11] and Linehan, et. al.,[12] have used model compounds to study the hydrogen exchange and/or C-C bond cleavage promoted by Fe or FeS surfaces. Their results all provide strong evidence for bond cleavage following transfer of a single hydrogen. The data of Wei et al. indicate that even at 300°C and in the presence of 1450 psi H_2, reaction of 1,1'-dinaphthylmethane is almost exclusively to produce naphthalene and 1-methylnaphthalene, with very little di- or tetra-hydronaphthalene derivatives. These researchers consider that the intermediate in the cleavage reaction is a surface-bound ipso radical,[10] generated by H-atom transfer to produce intermediates exactly analogous to those involved in solvent-mediated hydrogenolysis. However, the examples discussed above, where the presence of only a few heteroatoms in the coal structure bring ionic reactions into play, should make us alert to the possibility that the surface of an ionic solid may also be promoting reactions that involve electron transfer or charged intermediates.

The nature of the intermediates on various iron surfaces are of particular interest for two very important reasons. First, although cleavage is facile at 300°C for displacement of resonance stabilized radicals[10] (or perhaps cations), displacement of unstabilized radicals appears not to occur even at 400°C.[12] Clearly transfer of a single hydrogen to bring about cleavage of very strong methylene bridges between two aromatic clusters is rapid, whereas displacement of bridges of two or more atoms, where the departing fragment is not resonance stabilized, essentially does not occur on these catalysts. Thus, these surfaces evidently will not cleave diarylethane linkages, but these are in any case weak bonds that will homolyze readily during liquefaction . These surfaces will also not serve to cleave bridges of three or more atoms, but such linkages are susceptible to cleavage via H-abstraction—ß-scission. The catalysis will also not cause displacement of simple alkyl groups. Thus, it is clear that such catalysts have the potential to use hydrogen to cleave those linkages it may be most important to cleave, leaving the more labile linkages of two or more atoms to less "expensive" routes (or to occur at a more convenient time), and leaving totally untouched the simple alkyl groups whose displacement would only result in hydrogen consumption and the unwanted formation of methane or other light hydrocarbon gases.

The second reason why these intermediates are of practical interest derives from the fact that the hydrogen needed for the cleavage does not have to come, at least during the coal dissolution step, from high pressure hydrogen. Linehan et al. report[12] using 9,10-dihydrophenanthrene, rather than H_2 gas, as the source of surface hydrogen for model compound studies testing their dispersed iron catalysts. This result is very interesting, because researchers have from time to time explored the possibility of catalytic use of donor hydrogen, sometimes called "transfer hydrogenation." However, what has most often been found is that under conditions with no hydrogen overpressure, typical coal liquefaction catalysts, which of course are usually good hydrogenation catalysts, serve simply as an open valve for rapid dehydrogenation of the donor solvent, while providing very little catalytic aid to the liquefaction itself. Clearly what is needed is a catalyst that allows relatively facile H-transfer from a hydroaromatic to the catalyst surface, but does not allow facile recombination to H_2 and dissociation. In the simplest terms, this would merely require a catalyst or conditions under which the dissociatively adsorbed hydrogen has sufficiently low coverage (and/or low mobility) to limit recombination, but enough coverage to be active in causing single H-atom transfer to positions on aromatic clusters bearing linkages. Since the requirements for low coverage and high activity tend to be conflicting, a balance providing real-world catalytic utility may be difficult to find. Thus it is likely that an effort to substantially accelerate selective catalytic cleavage under conditions where there is no hydrogen overpressure will need to be aided by a better picture of the critical surface-bound species and their reactivity.

Examination of the data of Davis and coworkers[11] reveals an observation parallel to the exclusive displacement of resonance-stabilized groups, namely that isotopic exchange of aromatic hydrogens (e.g., on 1-methylnaphthalene), occurs without loss of a methyl fragment. However, this is not what would generally be expected were the surface intermediate an ipso-radical species. As shown in Table 1, the estimated rates of either unimolecular H-atom elimination or bimolecular removal of H-atoms via interaction with solution-phase species are substantially lower than estimated rates of methyl radical elimination (assuming that the thermodynamics of H-atom loss are essentially the same as those for solution-phase ipso-radical species). The differences would be even greater for elimination of ethyl radicals and other non-benzylic fragments.

Ades et al. have suggested[13] that the iron-sulfide-catalyzed cleavage of the model compound bibenzylnaphthylmethane involves one-electron oxidation to the radical cation, which then cleaves directly (preferentially giving a naphthyl- and a bibenzylmethyl fragment). However, Penn and Wang[14] have shown that generation of bona fide radical cations, either in solution or in the gas phase, leads preferentially to cleavage of the weakest bond in the original molecule (in this case the bibenzyl linkage) or secondarily to cleavage that gives the most stabilized benzylic fragment (in this case a naphthylmethyl fragment). This contrasts with the observed FeS-catalyzed cleavage, which gives preferential cleavage *between* the methylene linkage and the naphthalene ring.

Autrey et al., in one of the preceding papers in this symposium,[15] also invoke one-electron oxidation, but not direct cleavage of the radical cation. They suggest the inability of the cleavage intermediate to eliminate a simple alkyl fragment may reflect that fact that it actually is a cationic species resulting from electron transfer to the surface, followed by H-atom transfer to the substrate to generate the ipso-cation. Such a species might well exhibit the high selectivity observed for elimination of a benzyl fragment, as compared to a methyl fragment. However, this would be tantamount to an acid-cracking process, for which molybdenum and iron sulfide surfaces are not generally known. Furthermore, a mechanism involving elimination of benzylic cations (from either cation or radical-cation intermediates) would have to account for the absence of transalkylation products by invoking what amounts to a hydride transfer to the benzyl cation before it departs the surface. Thus it appears to us that neither direct cleavage of a radical cation nor formation and cleavage of an acid cracking intermediate offer very satisfactory explanations of the observed bond cleavage.

A partially satisfactory rationalization can be achieved by noting that application of the estimated cleavage rates (Table 1) to surface species requires qualification. The zeroth-order assumption of little change in the thermodynamics of the surface-bound species, relative to the same species in solution, is clearly an oversimplification. Preferential adsorption on the surface of course means stabilization, relative to the bulk solution-phase species. This stabilization will make more difficult the unimolecular elimination of a methyl radical, which will be less strongly bound on the surface than the larger and more polarizable ipso-intermediate. On the other hand, the heat of adsorption of H-atoms on the catalyst surface will very likely be more than that for the ipso intermediate, thus facilitating exchange of the H-atom back to the surface. Thus, by considering, at least in qualitative terms, the relative impacts of surface adsorption on the various species, we can achieve a gross rationalization of the observed fragmentation behavior on iron catalyst surfaces, as compared to that which has already been quantified in the gas phase and/or bulk solution.

Additional support for a surface-bound radical intermediate may lie in the details of the isotopic exchange results briefly described above. Dabbagh et al. report[11] not only the total extent of exchange, but also the fraction of total deuterium found at positions 2 through 8 on the 1-methylnaphthalene recovered from the high-temperature exchange and also from a lower temperature (100°C) acid-catalyzed exchange. The deuterium distributions, as shown in Table 2, are very similar in the two cases, *except* for the deuterium content at the position ortho- to the 1-methyl group.

The high temperature, surface-promoted exchange results in only ~9% of the deuterium being located at the 2-position, very similar to the 3-, 6-, and 7- positions, which are the least reactive in the molecule. In contrast, under acid-catalyzed exchange conditions, the 2-position has 30% of the deuterium, almost as much as the most reactive (4-) position. We tentatively conclude that the rapid exchange at the inherently unreactive 2-position under acidic conditions reflects marked stabilization by methyl of the partial positive charge at the 1-position that results from proton attack. In contrast, the minimal enhancement (by 1-methyl substitution) of iron-catalyzed exchange at the 2-position suggests that exchange there occurs via H-atom transfer, since the benefits of creating a tertiary radical center are *much* less than the benefits of creating a tertiary carbocation. This difference is illustrated by the relative enthalpy costs for generating secondary and tertiary cations and radicals ($\Delta\Delta H°_{298}$[cation-parent alkane (g)] is 16 kcal/mol greater for generation of the isopropyl cation than for generation of the t-butyl cation [from the respective alkanes], whereas the difference is only 2-3 kcal/mol for generation of the secondary and tertiary radicals[16]).

Although the above rationalization of observed cleavage selectivity and H-exchange patterns may remove any compelling need to invoke the generation and decomposition of positively charged hydrocarbon species on the iron surface, we believe the possibility of ionic intermediates should still be kept in mind. It is imprudent to simply assume that decomposition that is aided by adsorption on a surface that is even modestly ionic, and/or has some semiconductor character, does not involve either electron transfer or the formation of charged species. To the extent that the catalytically active surfaces (or edges) are not pure sulfides, but are some class of much more ionic mixed oxysulfides, or to the extent that iron vacancies (as often invoked for pyrrhotite) are present to provide the surface with electron donor/acceptor properties, the possibility of charged intermediates needs to be considered. Moreover, given the inability, via prior- or post- analysis of the inorganic phase, to make definitive statements about the nature of the active catalyst under the *actual reaction conditions*, more systematic use of model compound variations to probe the nature of the these catalysts is clearly in order. For instance, the possibility of reaction via cationic intermediates, such as that argued against above, could be further tested by comparing the catalytic decomposition of diarylmethanes to their diaryl ether analogs. Decomposition to give aryloxy cations should be distinctly less favored than decomposition to give arylmethyl cations, whereas decomposition to give aryloxy radicals would if anything be more favored than in the hydrocarbon analog.

There is also a fourth possibility that needs to be considered for these catalytic bond cleavages, namely that *net* H-atom attack might result from 1-electron reduction, followed by proton transfer to the radical ion. Although one-electron reduction is not such an obvious candidate with an iron-deficient surface like pyrrhotite that should show better acceptor, rather than donor, properties,[13] the exact surface (or edge) properties of a nominal pyrrhotite catalyst under reaction conditions are hardly well known. Such an electron-transfer, proton-transfer sequence could call into play both the electronic properties of the iron sulfide and the weakly acid character of surface sulfhydryl groups[17] to provide a catalyzed route to net H-atom transfer.

Suffice it to say at this point that (1) some species on the iron-oxygen-sulfur surface is bringing about selective C-C bond cleavage while utilizing hydrogen obtained from a donor solvent, (2) to do this without gross dehydrogenation of the solvent to H_2 could be very valuable, and (3) understanding the relationship between these surface species and the ipso-radical intermediates responsible for hydrogenolysis in the bulk donor solvent could be key to optimizing and exploiting such reactions.

SUMMARY AND CONCLUSIONS

Heteroatom functional groups, namely phenolic and ether oxygen, very likely play a key role in coal conversion by facilitating rapid transfer of hydrogen as a proton, both to promote bond cleavage and also to allow strong-bond formation. This proton-transfer may sometimes involve uncharged acidic species, such as keto-forms of phenols, which are common recombination intermediates, and sometimes cations that are formed by one-electron oxidation of radicals. The cleavage of certain oxygen-substituted diaryl ether structures, such as polyxylenol, may be promoted by protonation and reductive electron transfer, followed by facile elimination of an aryloxy radical fragment.

Thermal reactions of donor solvent and coal structures are relevant to catalytic processes first in the sense that these two classes of reactions can operate in a very complementary fashion. Two key examples are catalytic hydrotreatment of heavy oil and coal-oil coprocessing. In these two cases, improved use of catalyst allows higher operability temperature limits that make more effective use of thermal distillate generation processes.

Thermal reactions are also relevant to catalytic processes in the sense that the understanding of thermal bond cleavage processes that has been acquired in the last ten years provides a background for learning about the structure of intermediates on catalyst surfaces. Reexamination of data in the recent literature for model compound cleavage on iron sulfide surfaces results in the following observations.

- The observed products are *not* consistent with those generated from cleavage of bona-fide radicals cations, either in the gas phase or in solution.
- The observed bond cleavage, while consistent in itself with that known to occur for acid cracking, does not result in the transalkylation products commonly seen for solution-phase acid-catalyzed dealkylation.
- The H-exchange that occurs at un-substituted positions, which in all likelihood results from the same type of attack as does the ipso-displacement of linkages, shows a pattern consistent with H-atom, rather than H^+, attack.
- The increased selectivity for displacement of resonance-stabilized (e.g., benzylic) fragments, and the increased ratio of H-loss/methyl-loss, relative to the observed gas-phase or bulk-solution behavior, can be qualitatively rationalized by expected relative adsorption strengths on the catalyst surfaces.
- The data as yet provide no direct evidence about the possibility that *net* H-atom transfer could proceed by 1-electron reduction, followed by proton transfer to the radical ion. Such a sequence could be facilitated by both the electronic properties of the iron sulfide and the weakly acid character of surface sulfhydryl groups.

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Table 1

Estimated Rates of Unimolecular and Bimolecular Loss of Methyl Radical and H-atoms from 1-Methylnaphthalene Hydroaryl Radical Intermediates

Loss Process	Estimated Rate Constant (s^{-1})
Me• Elimination	1×10^4
H• Elimination	3×10^3
H-Loss by RD [a]	$<1 \times 10^2$
H-Loss by RHT [b]	$\leq 3 \times 10^3$

a. Pseudo-first-order rate constant for H-loss by radical disproportionation, where $[R\cdot]_{tot}$ is assumed to be dominated by the a-tetralyl radical, and is estimated to be less than 10^{-7} M in 90% naphthalene/10% tetralin.

b. Pseudo-first-order rate constant for H-loss by radical hydrogen-transfer, based on [naphthalene] = ~5M, and on a lower limit for RHT intrinsic activation energy of 17 kcal/mol.

Table 2

Substitution Patterns for Catalysis of Deuterium Exchange by Stainless Steel or Homogeneous Acids, from Data of Dabbagh et al.

1-Methylnaphthalene Ring Position	% of Total Aromatic Deuterium	
	SS-Catalyzed @ 385°C	Acid-Catalyzed @ 100°C
2	9	30
3	5	11
4	47	35
5	17	11
6,7	5	6
8	17	14